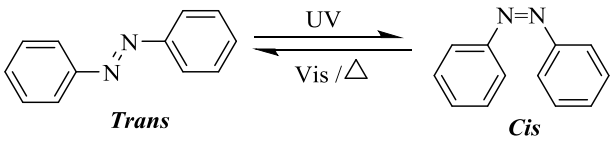
Introduction

Liquid crystals (LCs) are the intermediate states of matter in which the molecular order lie in between a crystalline solid and isotropic liquid. They possess a long-range order as in crystalline solid and mobility as in a liquid, and hence the name liquid crystals [1]. They are also called mesophases and the compounds that exhibit mesophases are known as mesogens. The fundamental requirement for a compound to be a mesogen is the shape anisotropy of the constituent molecules. LCs are broadly classified into two types: (i) thermotropic and (ii) lyotropic. Thermotropic LCs are obtained by the action of heat on a substance, whereas, lyotropics are formed by the action of a solvent on a solute. As this thesis deals with the synthesis and studies of some thermotropic LCs, we restrict our discussion only to this topic. Depending on the shape of constituent molecules, the thermotropic LCs are further classified into conventional and non-conventional LCs. The conventional LCs are formed by rod-shaped and disc-shaped molecules and the rest of the LCs falls under the non-conventional LCs, viz., bent-core, V-shaped, dimeric, phasmidic etc.

Molecular architecture is an important factor that governs the liquid crystalline properties of a compound. Thus, it is very important and interesting to study the relationship between molecular structure and liquid crystalline property. It is a challenging task for chemists to synthesise a mesogen with the required functionality and mesomorphic properties, as their combination generally results in the loss of one of these properties. The present thesis, deals with the design, synthesis and studies on the structure-property relationship of some thermotropic azo substituted compounds. Here, the structure-property relationship is investigated, mainly, with respect to the effect of different lateral substituents, linkage groups, central bending angle and the number of aliphatic chains present in the molecules.

The combination of photochromic and mesomorphic properties in the same molecules may render such materials useful for various practical applications. Azobenzene derivatives are the best examples for such purpose due to the simplicity involved in the synthesis and their ability to undergo fast, efficient and fully reversible photo-isomerisation [2-7], as shown below.



Thus, most of the compounds presented in this thesis are azo substituted ones and therefore, the photochromic properties of some of the compounds are also presented, in detail. Different types of compounds, viz., (i) rod-shaped (ii) bent-shaped (iii) V-shaped and (iv) dimeric compounds have been investigated by varying the molecular architecture, in a systematic way. These newly synthesised compounds are characterised by organic spectroscopic methods and elemental analysis. The liquid crystalline properties are investigated by using polarizing optical microscopy (POM), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and electro-optical (E-O) studies. This thesis constitutes of seven chapters, wherein, the first one is an introduction to the topic LCs and the work carried out in the subsequent chapters. The next five chapters deal with the experimental work carried out for this thesis, results and discussion and a summary of the observations. The last one, chapter 7, gives the conclusions and outlook of this thesis.

Chapter **2** deals with the investigations on structure - property relationship with respect to the lateral substituents and central bending angle of constituent molecules of a mesogen. Thus, some rod-shaped compounds were synthesised with different lateral substituents and then their central bending angle was changed, in a systematic way, to form bent-core and finally to V-shaped compounds. The compounds consisting of rod-like achiral molecules are known to

form classical Sm and N mesophases. Since the discovery of bent-core mesogens, several mesophases viz. B_1, B_2,..B_8, dark conglomerates etc. have been observed. However, among them, the electro-optical switching behaviour is observed only for some of the mesophases. Among such switchable mesophases, the B_5 mesophase is very scarcely found in the literature [8]. The first B_5 mesophase was observed in a bent-core compound in 1998 [9]. In the case of V-shaped compounds, earlier it was reported that such mesogens with acute angle, form only calamitic/classical mesophases, such as N, SmA, and crystal E phases [10, 11]. Nonetheless, of late, such compounds are also reported to form bent-core mesophases [12-14]. Till today, there is only one report in literature on a V-shaped compound exhibiting an orthogonal polar biaxial smectic A mesophase ($SmAP_A$), so far [13].

In the present investigation, it is observed that the rod-shaped compounds exhibit only one type of mesophase which is unidentified owing to their high transition temperatures and the bent-core compounds exhibit B_1 and B_2 mesophases. For the first time, a B_5 mesophase and a direct transition from the isotropic phase to the $SmAP_A$ mesophase is observed, enantiotropically, over a wide temperature range in V-shaped compounds. It is found that while the central bending angle of the molecules has a clear cut impact on the nature of the mesophases exhibited, the lateral substituents have hardly any effect, in such compounds.

Chapter **3** deals with several new bent-core salicylaldimine functionalised mesogens belonging to different homologous series. Interestingly, most of the compounds synthesised here are found to exhibit dark conglomerate (DC) mesophases, a scarcely observed phase among other bent-core mesophases. The most prominent characteristic of the DC phase is an optically isotropic texture or have little birefringence owing to a distortion of long-range periodic order [15, 16]. On rotation of the analyser by a few degrees relative to the polariser, the conglomerate domains appear alternately dark and bright. Depending on the local

structure of these DC phases and packing density of bent-core molecules, they are classified into fluid spongy, helical nano-crystallite (HNC) and helical nano-filament (HNF) mesophases [15-18]. In the present investigation, the structure - property relation has been studied with respect to the different lateral substituents, different linkage groups and the presence of salicylaldimine group at different locations of the bent-core molecules. All the compounds are found to be liquid crystalline exhibiting different types of DC and/or B_2 mesophases depending on, mainly, the location of salicyladimine group in the molecular architecture.

Chapter **4** deals with the dimeric compounds. As mentioned earlier, the molecular architecture is an important factor for a compound to be a mesogen. This molecular structure may be modified by several ways. One such method is the formation of dimers. It is said that, such dimers may act as model compounds for liquid crystalline polymers [19-22]. The liquid crystalline dimers obtained by connecting two monomers through a flexible spacer have attracted more attention due to the novelty in their mesomorphic properties when compared to their corresponding monomers. Different kinds of monomers, such as, bent-core, calamitic, discotic, etc., have been utilised to obtain symmetrical and non-symmetrical dimers. In this chapter, the structure – property relationship of two series of symmetrical dimers, obtained by using V-shaped and Bent-shaped monomers, has been investigated. It is observed that the dimers composed of V-shaped monomers are found to be non - liquid crystalline, whereas, those composed of bent-core monomers exhibit some highly ordered mesophase.

Chapter **5** deals with the bent-core azo mesogens. This work is a continuation of the work done, previously, by Prasad *et al*. [23] from our laboratory. In the present study, the influence of alkyl and alkoxy chain length on the photoisomerization properties has been studied in addition to the liquid crystalline behaviour. These compounds are found to exhibit B_1, B_2 and

an unidentified mesophase. It was observed that the compounds with alkoxy chains have higher thermal back relaxation time when compared to those with alkyl chains, wherein the relaxation time was extremely slow or even hindered. An optical storage device also has been fabricated by doping this alkoxy compound into a nematic liquid crystal.

Chapter **6** deals with the cholesteric LCs (CLCs), also known as chiral nematic (N*) LCs. CLCs are very important from the application point of view. They are mainly used in thermal sensors. The objective of the present investigation was to obtain a photo-responsive room temperature CLC having a wide mesophase range. Such materials may be used in optical storage devices and related applications. Towards this end, three different series of azo substituted compounds were designed and synthesized. These three series differ from each other with respect to the number of alkoxy chains present in their molecular structures. They exhibit N* and SmC* mesophases. It was observed that the compounds with one alkoxy chain exhibit SmC* and N* mesophases whereas those with two alkoxy chains show only N* mesophase. The compounds with three alkoxy chains also exhibit only N* but, interestingly, here, the mesophase is room temperature for most of the homologues unlike the previous compounds with two alkoxy chains. The highest mesophase range obtained for this mesophase in this series is above 160^{o} and this is the widest mesophase range known till today for N*, in the literature. An optical storage device has been fabricated using this CLC. An Indian patent has also been filed for the novel results obtained during these studies.

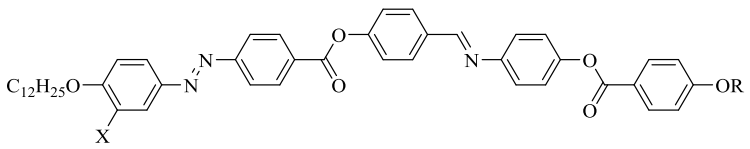
All the chapters in this thesis, except the first and last ones, begin with a brief literature survey of the type of compounds studied in the respective chapters. The first chapter gives an introduction and the last one gives a conclusion and outlook for the thesis work. A chapter-wise overview of the important aspects covered in this thesis is as follows:

Chapter 1: Introduction

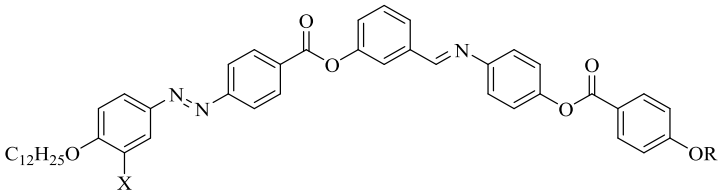
This chapter begins with a brief introduction to the topic LCs and their classification. Further, it focuses on the different types of molecular architectures studied in this thesis, viz., rod-shaped, bent-shaped, V-shaped, dimeric and cholesterol based azo compounds with a detailed introduction to each of these topics.

Chapter 2: Rod- to bent- to V-shaped mesogens: A systematic study on the effect of bend-angle on mesogenic property

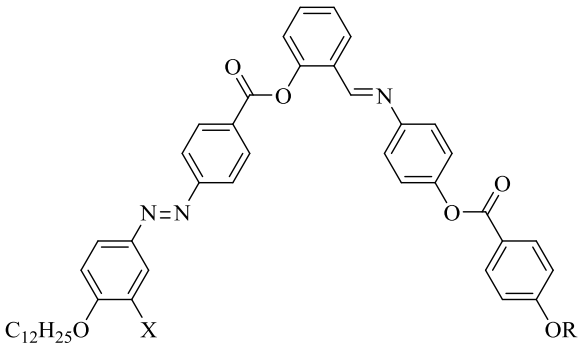
This chapter deals with the structure-property relationship, when the molecules of a compound are bent from a conventional to non-conventional shape. In addition, the effect of different types of lateral substituents on the mesomorphic properties are also studied. Thus, to begin with, a series of rod-like azo compounds were synthesised (series 2.A and their laterally substituted compounds) and then their bent (series 2.B and their laterally substituted compounds) and V-shaped (series 2.C and their laterally substituted compounds) variants were also designed and synthesised. The molecular structures of these compounds are as follows:



$R = C_nH_{2n+1}$		
Series 2.A	X = H	n = 10, 12, 14, 16
2.A-12-Cl	X = Cl	n = 12
2.A-16-Cl	X = Cl	n = 16
2.A-12-F	X = F	n = 12
2.A-16-F	X = F	n = 16
2.A-12-CH_3	X = CH_3	n = 12
2.A-16-CH_3	X = CH_3	n = 16



R = C_nH_{2n+1}		
Series 2.B	X = H	n = 4, 6….16
2.B-8-Cl	X = Cl	n = 8
2.B-10-Cl	X = Cl	n = 10
2.B-12-Cl	X = Cl	n = 12
2.B-8-F	X = F	n = 8
2.B-10-F	X = F	n = 10
2.B-12-F	X = F	n = 12
2.B-8-CH_3	X = CH_3	n = 8
2.B-10-CH_3	X = CH_3	n = 10



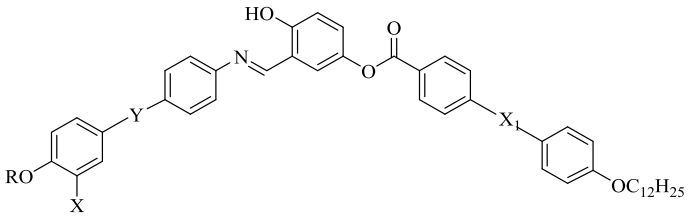
R = C_nH_{2n+1}		
Series 2.C	X = H	n = 4, 6….12
2.C-6-Cl	X = Cl	n = 6
2.C-12-Cl	X = Cl	n = 12
2.C-6-F	X = F	n = 6
2.C-12-F	X = F	n = 12
2.C-6-CH_3	X = CH_3	n = 6
2.C-12-CH_3	X = CH_3	n = 12

In all the above series, the chain length at one end of the molecule was kept fixed as -$OC_{12}H_{25}$ and the chain length at the other end was varied systematically. Thus in each series, four variants were synthesised by substituting different lateral substituents on the

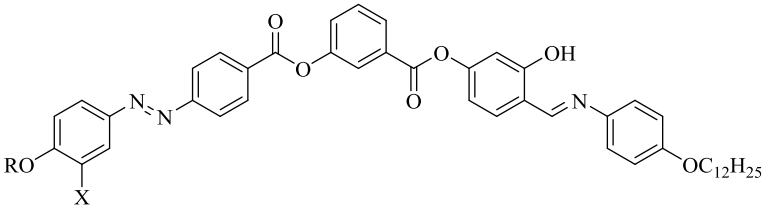
terminal phenyl ring of one of the wings. Thus, X in the above figures is varied as X = H, Cl, F, and CH_3. The transition temperatures of rod-shaped compounds are very high compared to bent-core and V-shaped compounds, exhibiting only one type of mesophase which is unidentified. The bent-core compounds exhibit B_1 and B_2 mesophases irrespective of the type of lateral substituents present, whereas in the case of V-shaped compounds the lateral substituents affected the nature of the mesophases exhibited. Thus, when X = H, the V-shaped compound exhibit a biaxial orthogonal smectic mesophase ($SmAP_A$) and this is the first observation of the direct transition from the isotropic phase to a $SmAP_A$ mesophase in such compounds. This is the first compound wherein this mesophase is characterised completely including the switching time. The fluoro substituted V-shaped compound exhibits a B_5 mesophase which shows the ferroelectric switching behaviour. This is the first report of a V-shaped mesogen exhibiting a B_5 mesophase. In addition to these two mesophases, the V-shaped compounds exhibited some monotropic mesophases as well which are unidentified owing to their metastability. The combination of bend–angle and lateral fluoro substituted molecular architecture appears to play an important role in the formation of $SmAP_A$ mesophase. Such mesogens may be utilised for designing novel electro-optic devices with fast switching time.

Chapter 3: Achiral bent-core salicylaldimine compounds exhibiting dark conglomerate and B_2 mesophases: Effect of linkage groups and lateral substituents

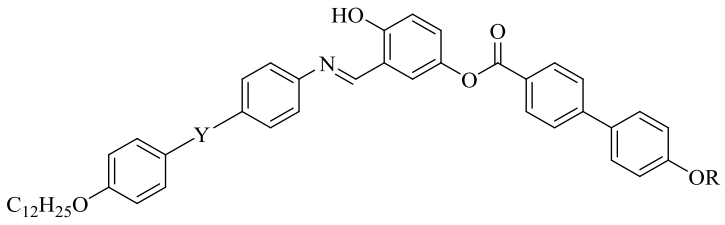
This chapter describes the design and synthesis of four new homologous series of bent-core salicylaldimine compounds, viz., series 3.A, 3.B, 3.C and 3.D in addition to two biphenyl derivatives of these compounds (compounds 3.E and compounds 3.F). The molecular structures of these compounds are as follows:



$R = C_nH_{2n+1}$				
X_1 = -OOC-	Y = -N=N-	X = H	n = 12, 14, 16	Series 3.A
X_1 = -OOC-	Y = -N=N-	X = F	n = 12	3.A-12-F
X_1 = -OOC-	Y = -N=N-	X = Cl	n = 12	3.A-12-Cl
X_1 = -N=N-	Y = -COO-	X = H	n = 12, 14, 16	Series 3.B
X_1 = -N=N-	Y = -COO-	X = F	n = 12	3.B-12-F
X_1 = -N=N-	Y = -COO-	X = Cl	n = 12	3.B-12-Cl
X_1 = -N=N-	Y = -N=N-	X = H	n = 12, 14, 16	Series 3.C
X_1 = -N=N-	Y = -N=N-	X = F	n = 12	3.C-12-F
X_1 = -N=N-	Y = -N=N-	X = Cl	n = 12	3.C-12-Cl



$R= C_nH_{2n+1}$		
X = H	n = 12, 14, 16	Series 3.D
X = F	n = 12	3.D-12-F
X = Cl	n = 12	3.D-12-Cl



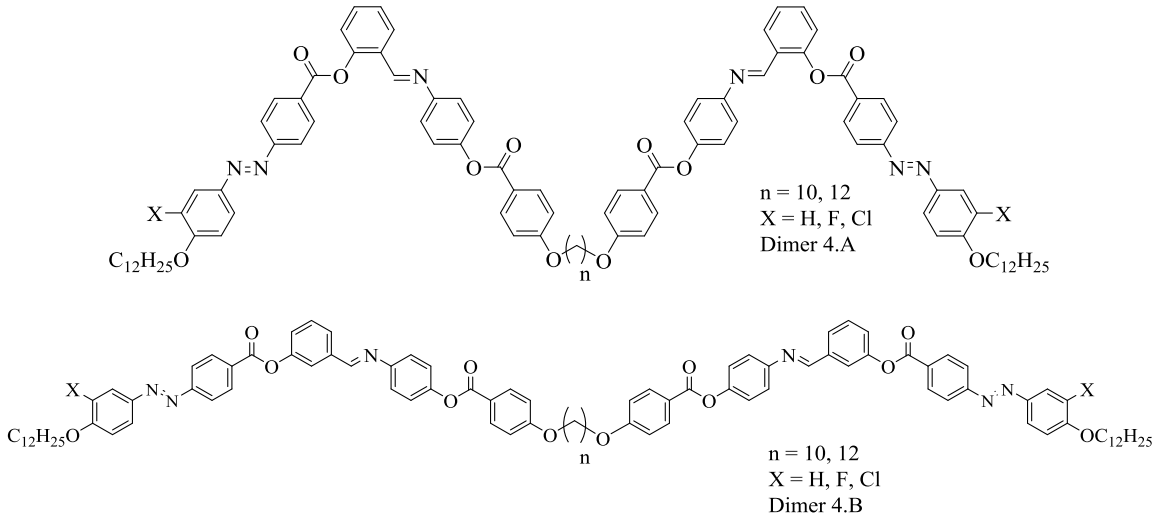
R = C_nH_{2n+1}			
Y = -COO-	X = H	n = 12, 14	Compounds 3.E
Y = -N=N-	X = H	n = 12	Compound 3.F-12.
Y = -N=N-	X = Cl	n = 12	Compound 3.F-12-Cl.

The homologues of series 3.A, 3.B, 3.C, and compounds 3.E and 3.F, wherein the salicylaldimine group is present at the center of the bent-core, exhibit DC mesophases. Series 3.A exhibits only DC mesophases, whereas series 3.B and 3.C exhibit a B_2 mesophase when X = H and a DC mesophase when X = F/Cl. The homologues of series 3.D, wherein the salicylaldimine group is present in one of the wings of the bent-core molecules, exhibit only a B_2 mesophase, irrespective of the nature of the lateral substitution. All the compounds exhibiting a DC mesophase, except the biphenyl derivatives, are also found to form chiral crystalline phases which are confirmed by the POM and further by circular dichroism studies. The electro-optical observations in conjugation with the XRD results, revealed the nature of the mesophases exhibited by these compounds as, DC_1* is of sponge type, DC_2* is of HNC type and B_2 is SmC_aP_A in nature wherein only DC_1* and B_2 mesophases are switchable.

Chapter 4: Azo functionalised symmetric dimers : Synthesis and mesomorphic properties

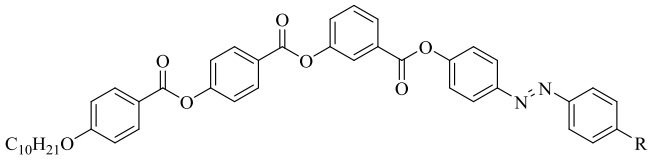
This chapter describes the design and synthesis of two different types of symmetrical dimers, viz., dimers 4.A and 4.B as shown below. The dimer 4.A is composed of V-shaped monomers connected through a flexible alkylene spacer, whereas the dimer 4.B is composed of bent-core monomers connected through a flexible alkylene spacer. The structures of these

dimers differ from each other only with respect to the central bending angle of their monomeric unit. The alkoxy chain length at one end of both the dimers are fixed as $–OC_{12}H_{25}$ and the spacer chain length is varied as n = 10 and 12. The monomeric units in these dimers are laterally substituted with X = H, F and Cl. We found that all the dimmers, 4.A, are non-mesomorphic whereas some of the dimers, 4.B, are mesomorphic exhibiting a highly ordered unidentified mesophase.



Chapter 5: Synthesis, mesomorphic and photoswitching properties of bent-core azo mesogens: Influence of alkyl and alkoxy chains on photo-responsive behaviour

The investigations presented in this chapter are a continuation of the previous work reported by Prasad *et al*, [23]. In the present study two new series of bent-core azo compounds, series 5.A and 5.B are synthesised, just by a slight modification of compounds reported earlier [23]. The molecular structures of these compounds are as follows:

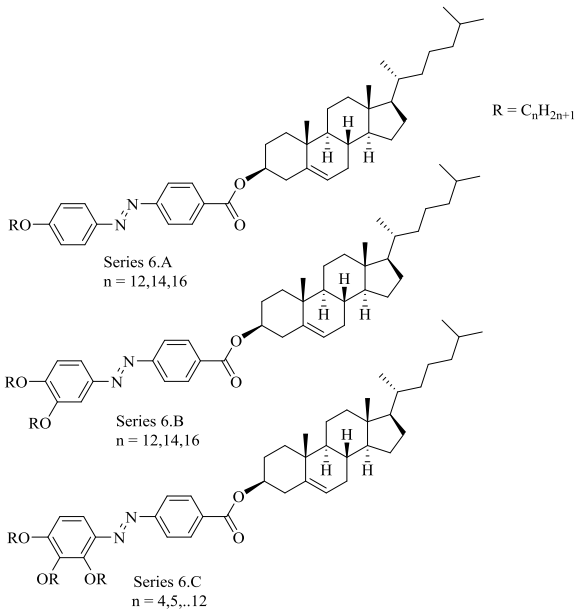


Series 5.A	$R = C_nH_{2n+1}$	n = 4, 6, 8, 10, 12
Series 5.B	$R= OC_nH_{2n+1}$	n = 4, 6, 8, 10, 12

As can be seen, in both the series, 5.A and series 5.B, the chain length at one end of the molecules is kept constant as $-OC_{10}H_{21}$ and the chain length at the other end is varied, systematically. Series 5.A has alkyl chain at one end and alkoxy chain at the other end, whereas, series 5.B has alkoxy chains on both the ends. These compounds exhibit mainly B_1, B_2 mesophases. The photoisomerisation study, both in solution and thin film, showed that the compounds with alkoxy chain have excellent thermal back relaxation as compared to those with alkyl chains. Therefore, a representative compound from the alkoxy series was chosen to fabricate an optical storage device and tested for the efficiency. The constructed optical storage device shows a very good contrast between bright and dark states. Thus, the proper tuning of these bent-core azo mesogens may be useful for the creation of long-term optical storage devices.

Chapter 6: Photo-responsive room temperature cholesteric liquid crystals: Synthesis and characterisation

This chapter describes the design, synthesis and characterisation of three series of cholesterol- based compounds, viz., series 6.A, 6.B and 6.C. The molecular structures of these compounds are as follows:



As can be seen here, the structure - property relationship has been studied as a function of the chain length as well as the number of alkoxy chains present in the molecules. Thus, Series 6.A has a single alkoxy chain, 6.B has two alkoxy chains and 6.C has three alkoxy chains in their molecular structure. It was observed that the compounds with one alkoxy chain exhibit SmC* and N* mesophases, whereas, those with two alkoxy chains show only N* mesophase. The compounds with three alkoxy chains also exhibit only N* and interestingly, it is a room temperature mesophase for most of the homologues. The highest mesophase range obtained for this phase in this series is 167^{o}C from room temperature and this is the widest mesophase range known till today for N*, in the literature. A device has been fabricated using this CLC.

Chapter 7: Conclusions and outlook

This thesis describes the design, synthesis, characterisation and mesomorphic properties of some thermotropic azo substituted mesogens. Mainly, the relationship between the molecular structure and mesomorphic properties have been studied. During the investigations, it is observed that a careful tinkering of the molecules can lead to novel mesogenic properties in newly synthesised compounds. Thus, some of the important results obtained during the studies are as follows:

The first V-shaped compound exhibiting a direct transition from the isotropic to $SmAP_A$ phase has been synthesised. This is the first compound wherein a $SmAP_A$ mesophase has been characterized completely, including switching time. In a similar way, the first V-shaped compound exhibiting a B_5 mesophase has also been synthesised and characterised. Many of the dark conglomerate liquid crystals synthesised, retained their chirality even in their crystalline states which is a very rarely observed phenomenon and of technological importance.

The photoisomerization studies on bent-core azo compounds indicated that the compounds with alkoxy chain have excellent thermal back relaxation as compared to those with alkyl chains. An optical storage device constructed by doping this alkoxy compound into a nematic liquid crystal, showed a very good contrast between the bright and dark states.

Cholesterol-based azo compounds with three alkoxy chains exhibited room temperature N* phase with a very wide mesophase range. An optical storage device has been fabricated using this CLC which showed a very good contrast between the bright and dark states.

Thus, most of the compounds reported in this thesis exhibit liquid crystals that are of interest both from fundamental and application point of view.

Some of the results presented in this thesis are published in the following international journals:

1. The first examples of V-shaped compounds exhibiting a B_5 mesophase and a direct transition from the isotropic to a polar biaxial smectic A mesophase.
   R. S. Hegde, J. Kumar, V. Prasad, M. Monika, *J.Mol.Liq*., **249**, 97-105 (2018).

2. Achiral bent-core salicylaldimine compounds exhibiting dark conglomerate and B_2 mesophases: Effect of linkage groups and lateral substituents.
   R. S. Hegde, J. Kumar, V. Prasad, *Liq. Cryst*., **46** (7), 1091-1107 (2019).

3. Influence of alkyl and alkoxy groups on photo-responsive behaviour of bent-core azo mesogens: Synthesis, mesomorphic and photoswitching properties.
   R. S. Hegde, B. N. Sunil, G. Hegde, V. Prasad, *J.Mol. Liq*., **309**, 113091 (2020).

Patent: Cholesteric liquid crystal and device thereof.
Veena Prasad, Nagaveni N.G., Gurumurthy Hegde and Rekha S. Hegde,
Appln. No. 201941036986 (Indian patent granted on 20-09-2021).

Presentation in Conferences/ Symposium/ Workshop

1. Poster presentation at National level Symposium, Materials Characterisation and Manufacturing (MCM-2016) at Goa University, Goa, during 18th and 19th August 2016. Topic: "Rod – to bent – to V-shaped mesogens: A systemic study of relationship of molecular structure to liquid crystalline property".

2. Poster presentation at DST-INSPIRE Fellowship Review Meeting held in Gandhi Institute of Technology and Management (GITAM) University, Bengaluru Campus, during 13-15 June 2019. Topic: "Studies on Some Non-conventional Liquid Crystals: Synthesis and Mesomorphic Properties".

Other publication:

1. Porous carbon nanoparticles dispersed nematic liquid crystal: Influence of the particle size on electro-optical and dielectric parameters.
   G. Pathak, R. S. Hegde, S. S. Punjalkatte, T. Rujiralai, G. Hegde, V.Prasad (2021), *Liq Cryst*., DOI: 10.1080/02678292.2021.1988740.

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